

REVERSE RADICAL DISPROPORTIONATION: A MECHANISTIC STUDY

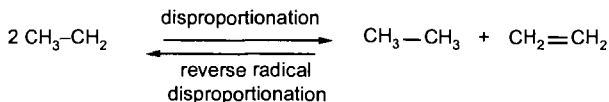
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INTRODUCTION

Radical disproportionations are well known radical destroying processes. The reverse reaction, accordingly, generates free radicals e.g. from an alkene and a hydrocarbon:



Despite a few early references (1) the scope and the mechanistic details of reverse radical disproportionations (retrodisproportionations) have been investigated only recently. In this context it was suggested that reverse disproportionations are important components to the complex network of reactions which are responsible for coal liquefaction processes (2) but also to synthetic dehydrogenations by quinones (3) or nitro compounds (4). In addition there is evidence which supports the assumption that NAD(P)H-reductions in the cell are initiated by reverse disproportionation (1,3).

EXPERIMENTAL

The methodology and the materials were described previously in detail (5).

RESULTS AND DISCUSSION

The mechanistic study which was performed in our laboratory concentrated in the beginning on the reactions of 9,10-dihydroanthracene (DHA), xanthene, acridane and N-methylacridane and a series of similarly structured hydrocarbons with weak C-H-bonds and α -methylstyrene as hydrogen acceptor. Then, in addition, a series of substituted styrene, cyclic dienes and aromatic hydrocarbons like azulene or polyacenes were included. These reactions are performed generally in the temperature range from 200 – 350° C. The reactions lead usually to quantitative transformations of starting materials. From this investigation, which will be reviewed briefly in this preprint, the three-step non chain radical mechanism of Scheme 1 was suggested

If the radicals formed from the donor in step 1 cannot disproportionate, alternative termination reactions are observed, frequently by participation of the solvent. In the case of styrene as an acceptor the DHA-derived radicals do add to another styrene molecule and a formal addition product of DHA to styrene is isolated (an-reaction) (6).

The following results support the suggested mechanism:

1. When the H-donors are varied, logk decreases proportionally with the increasing C-H-bond strength (Polanyi-relationship)
2. The activation enthalpies ΔH^\ddagger are a few kcal smaller than the reaction enthalpies of the rate determining retrodisproportionation step and they correlate linearly with each other (thermochemical kinetics) (7).
3. Solvent effects are small (<factor 10) and they do not correlate with solvent polarity.
4. Polar substituents in the acceptor (subst. α -methylstyrenes) or donor (xanthene or acridane vs. DHA or substituted DHA) are also small (< factor 10).
5. When deuterated donors are used no deuterium incorporation into the starting acceptor is found in most examples proving that step 1 is irreversible. The kinetic isotope effects

in these experiments $k(H)/k(D)$ are close to the maximal expected values at a given temperature.

6. The observation of an *isokinetic relationship* over a wide range of reactivity supports the assumption that no change of mechanism is occurring within this series.
7. The existence of free radical intermediates and their structures are shown by epr, by spin trapping, by radical clock experiments and by the observation of other radical rearrangements e.g. the azulene - naphthalene rearrangement (8).

A phenomenon which may be of importance in coal liquefaction processes is the observation that the H-transfer reaction of e.g. DHA to α -methylstyrene is strongly enhanced by the addition of a hydrocarbon with a weaker C-H bond (e.g. 7H-benz(de)anthracene) which is not used up during the overall reaction. This reaction, therefore, can be performed at temperatures as low as 200 – 230° C instead of 300° C when a „catalyst“ of this type is added (9). Fullerenes like C_{60} or C_{70} are transfer hydrogenated with DHA in a specific way to the partially hydrogenated products $C_{60}H_{16}$, $C_{60}H_{36}$ and $C_{70}H_{36}$ (10). The mechanistic criteria discussed above apply also to quinone oxidations of acridanes or N-subst.-nicotinamides. This suggests, that biochemicals NAD(P)H-reductions are also initiated by retrodisproportionation.

CONCLUSIONS

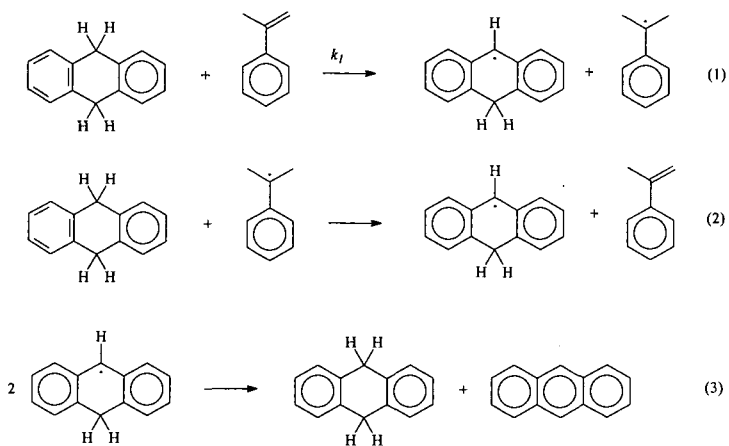
Retrodisproportionations are a class of important free radical reactions which have been unduly neglected for a long time. They are responsible in particular for high temperature hydrogen transfer reactions e.g. in coal liquefaction processes and their mechanisms are well understood now. The quantitative kinetic investigations should allow predictions for simulations of complex high temperature radical reactions of hydrocarbons.

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Scheme 1. Mechanism Proposed for Transfer Hydrogenation with DHA.